Spectroscopy of Mass/Charge Selected Cations and Anions in Helium Droplets

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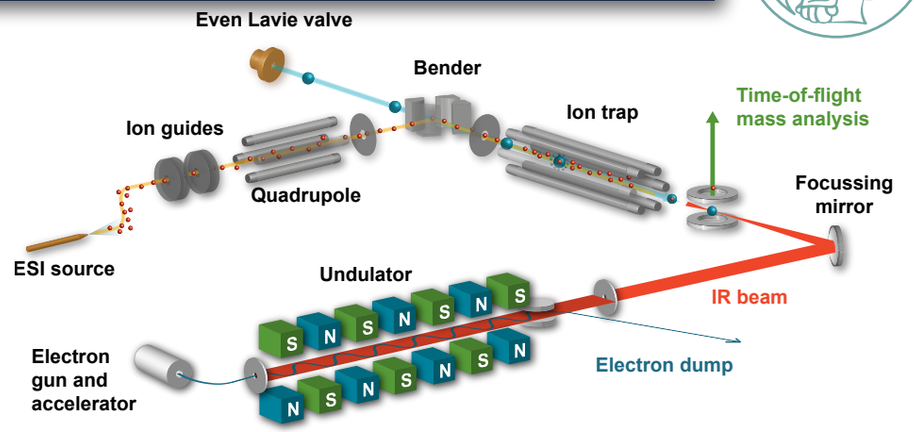
der
Max-Planck-Gesellschaft

Outline

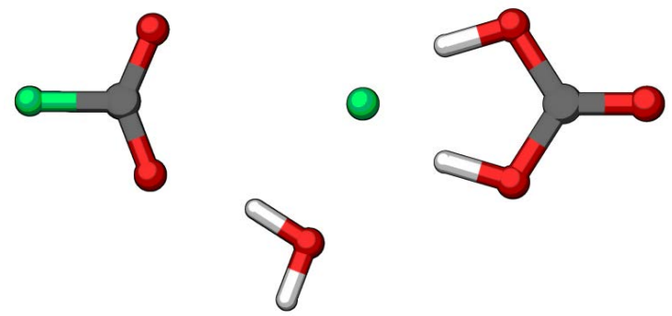
IR Spectroscopy in He Nanodroplets

- m/z selected cations and anions



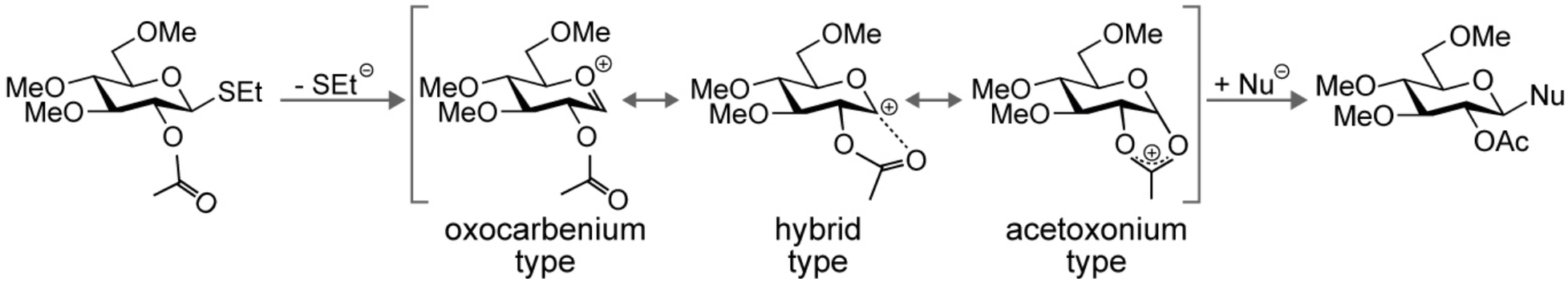
Fluoride Chemistry

- F^-, and its reactivity towards CO_2 and H_2O



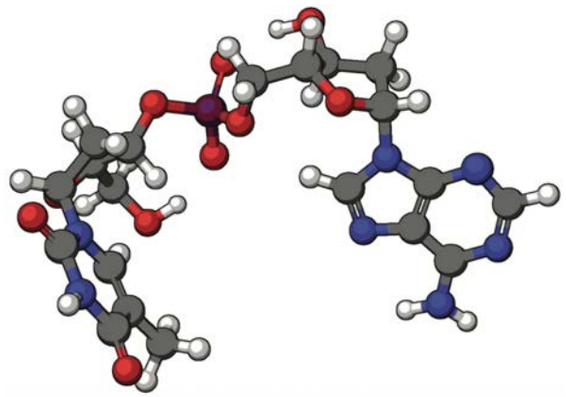
Glycosyl Cations

- Characterisation of an important reaction intermediate



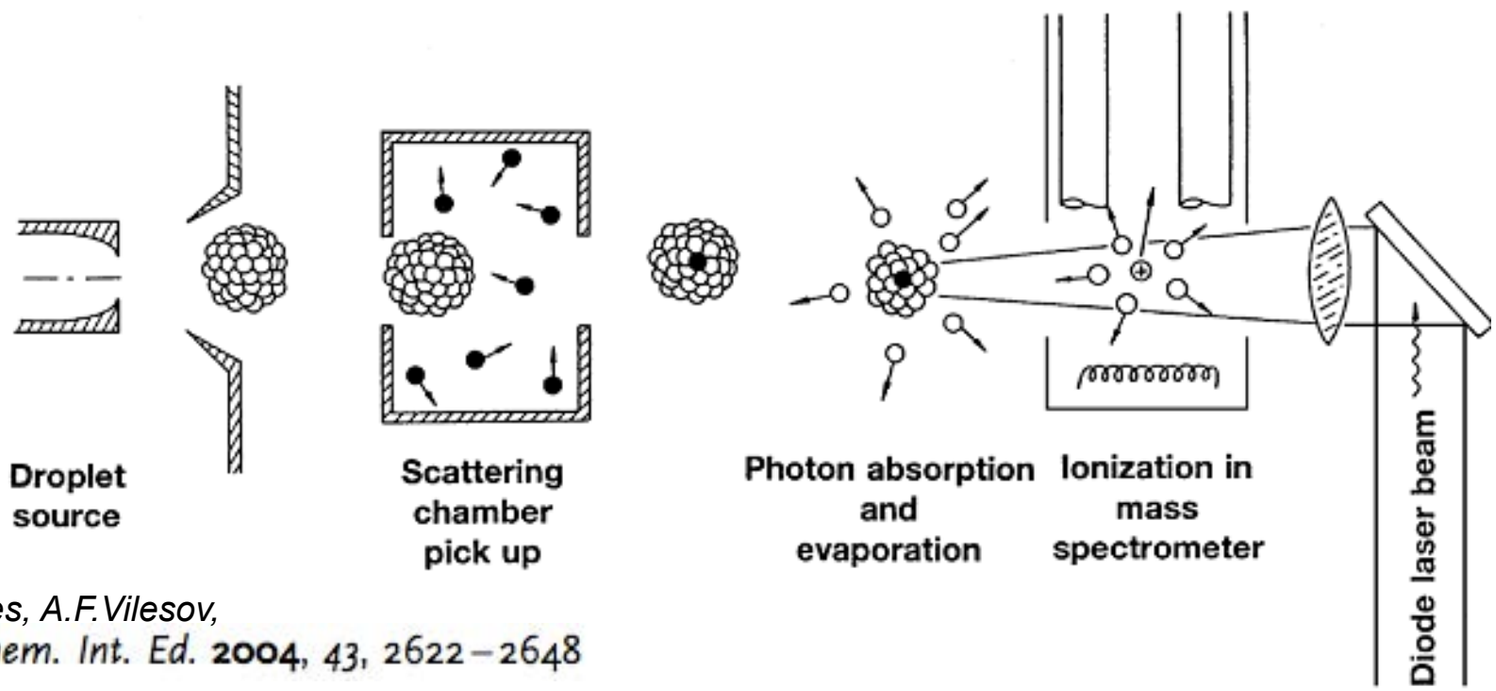
Dinucleotide dTpdA

- Probing thermal equilibria



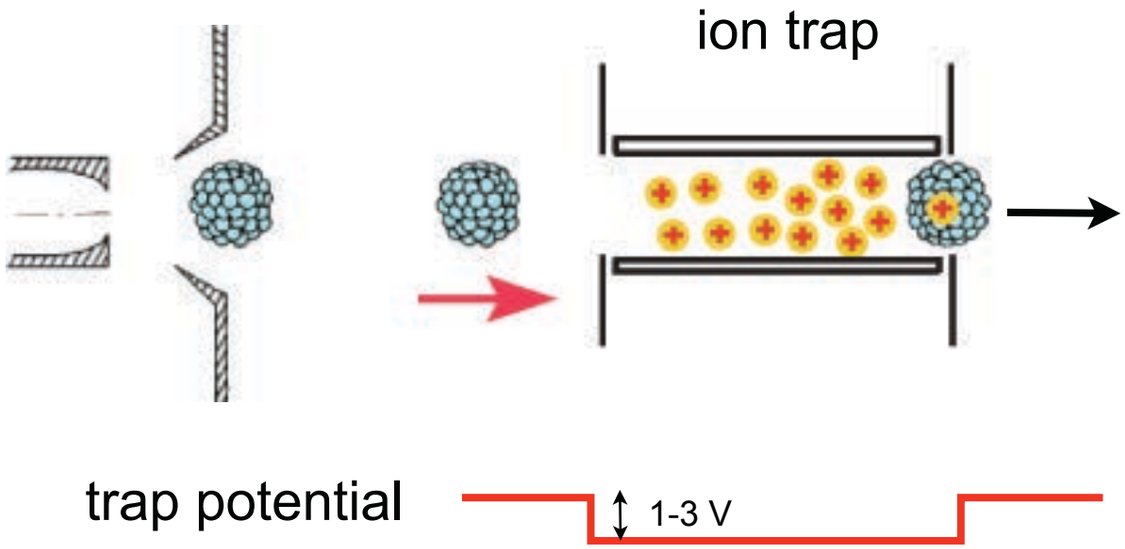
Pickup by liquid helium droplets

Pick-up of neutral species from a gas cell

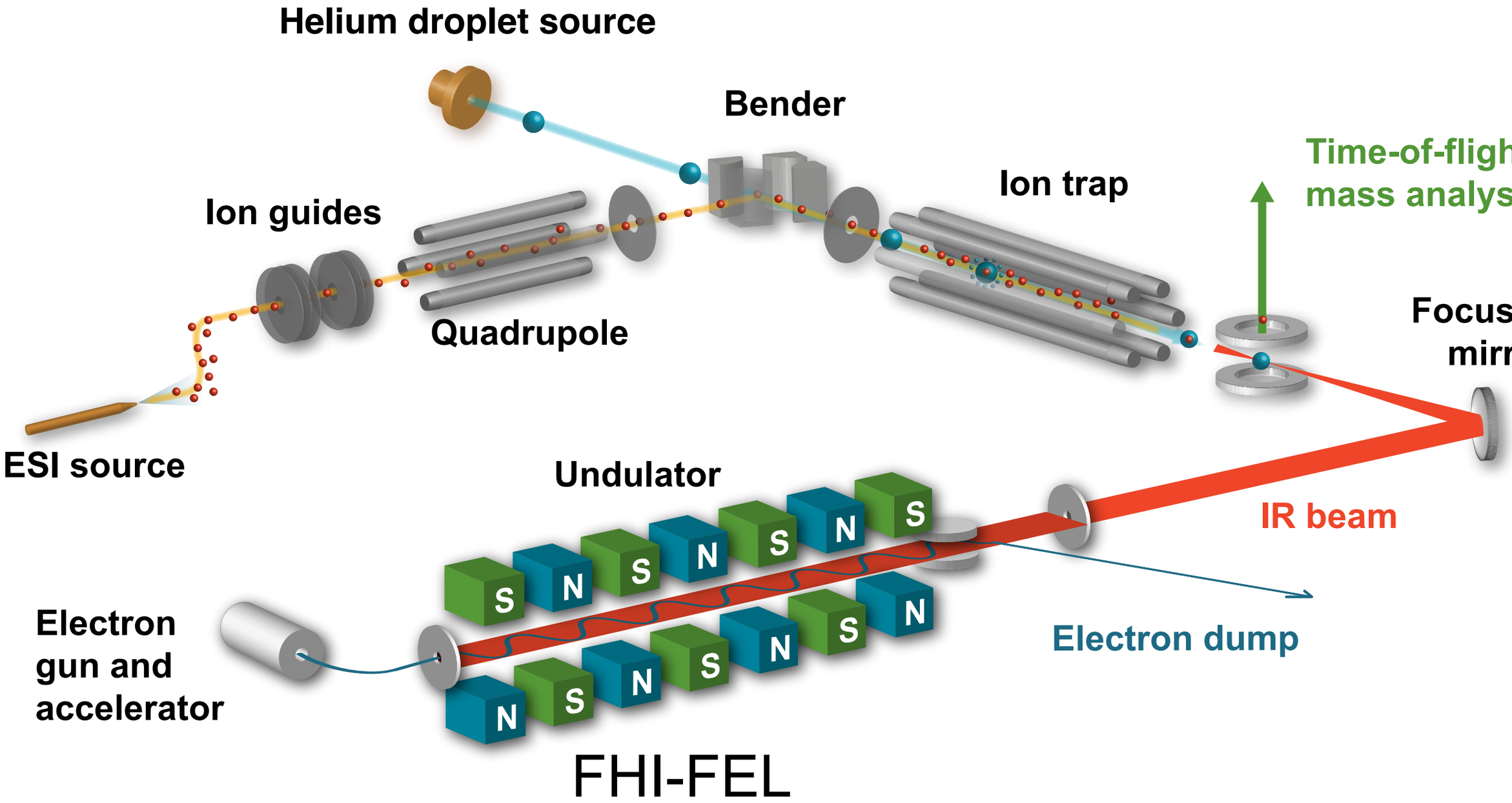


J.P.Toennies, A.F.Vilesov,
Angew. Chem. Int. Ed. **2004**, *43*, 2622–2648

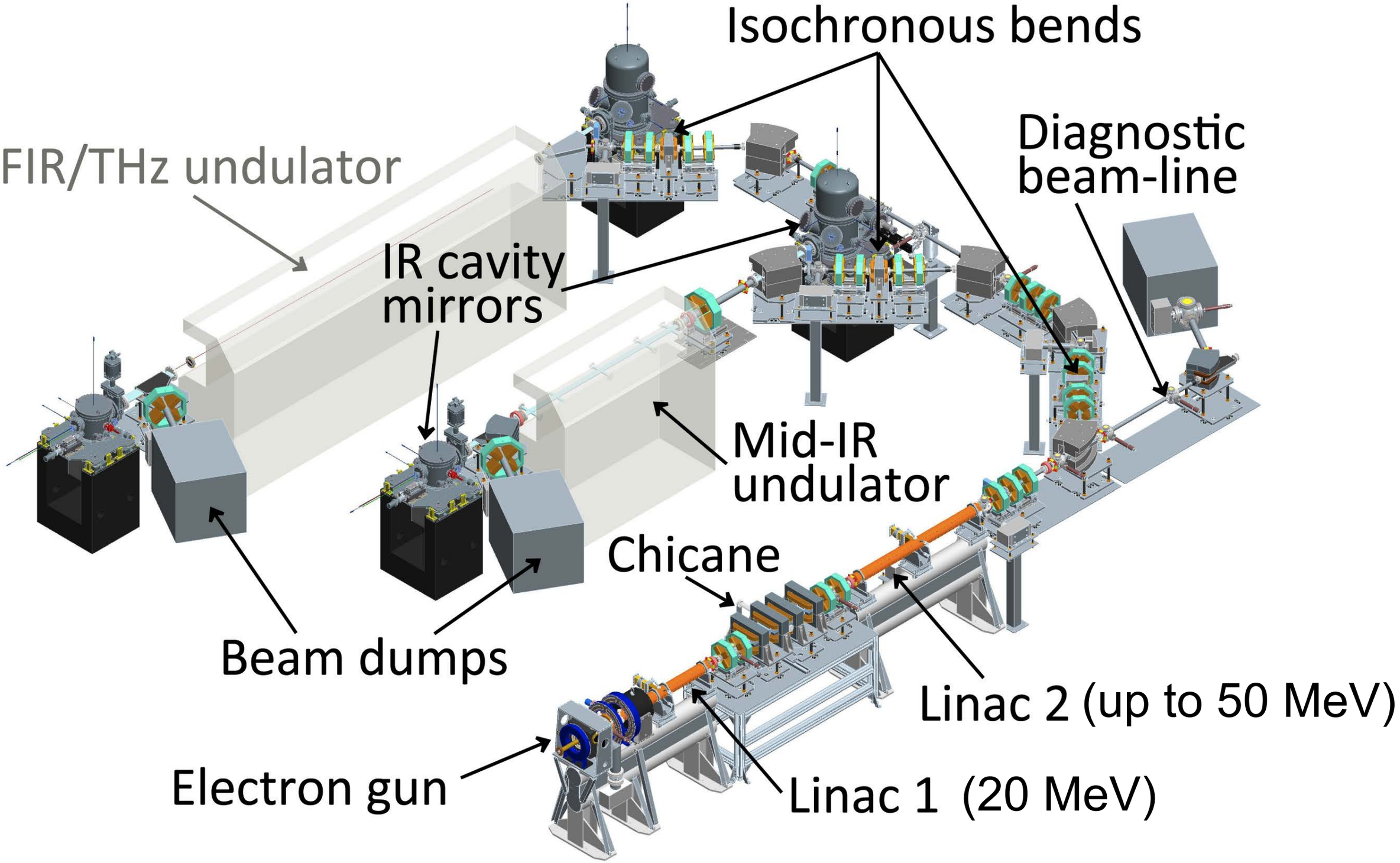
Pick-up of ions from a linear ion trap



Liquid helium droplet setup

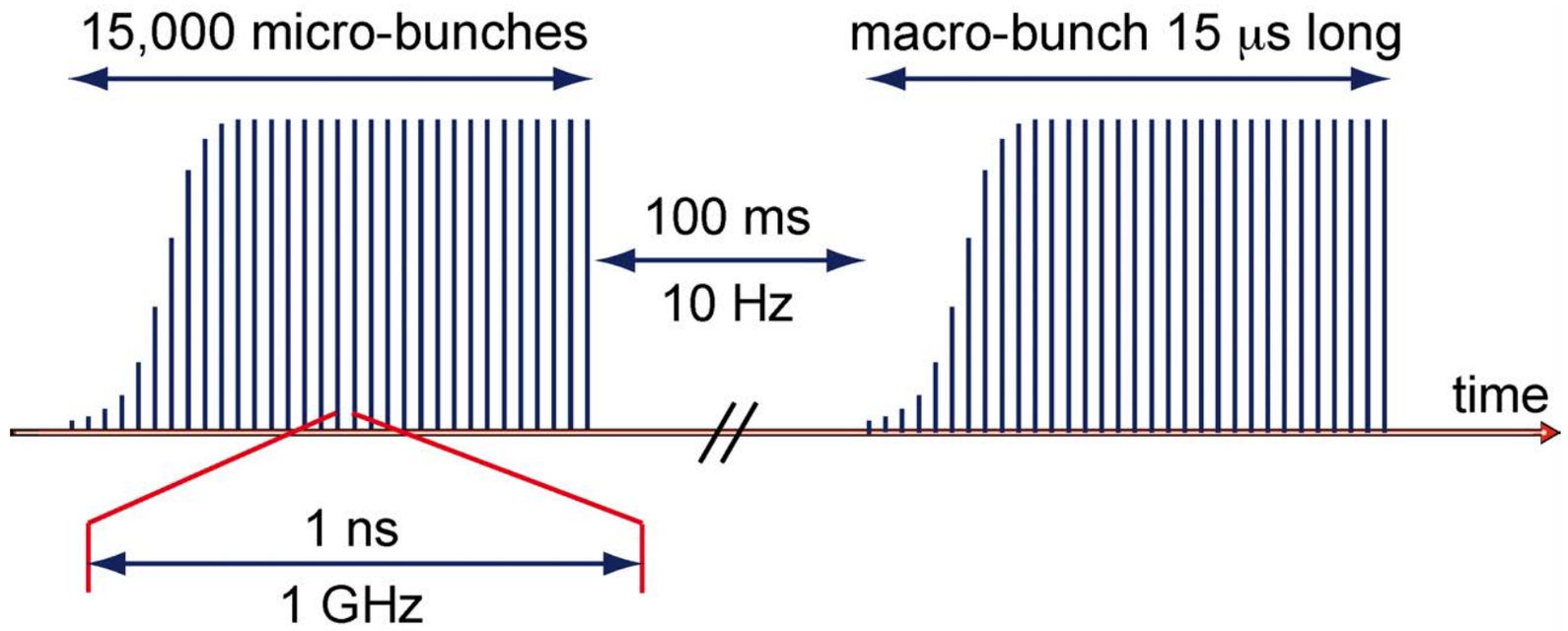


The FHI FEL


Isochronous bends
FIR/THz undulator
IR cavity mirrors
Diagnostic beam-line
Mid-IR undulator
Chicane
Beam dumps
Linac 2 (up to 50 MeV)
Electron gun
Linac 1 (20 MeV)

Specifications

The time structure of IR output given by electrons: micro-pulses and macro-pulses



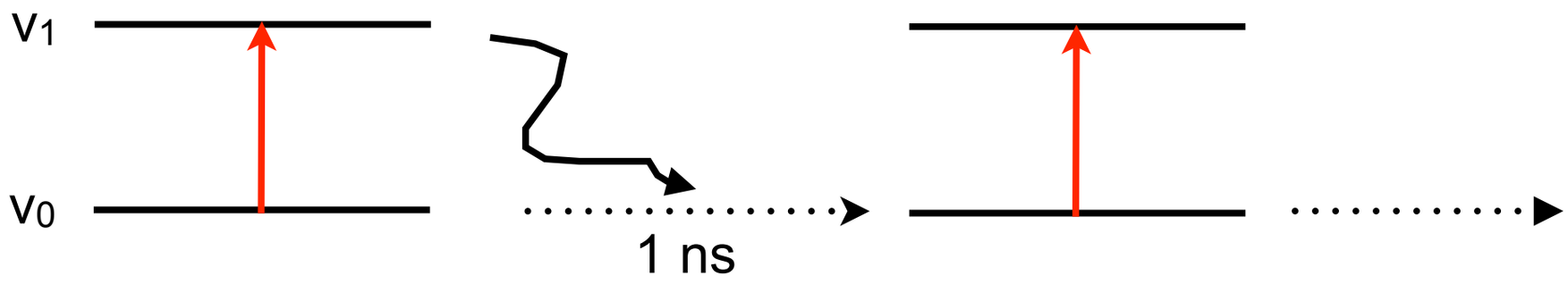
IR output:

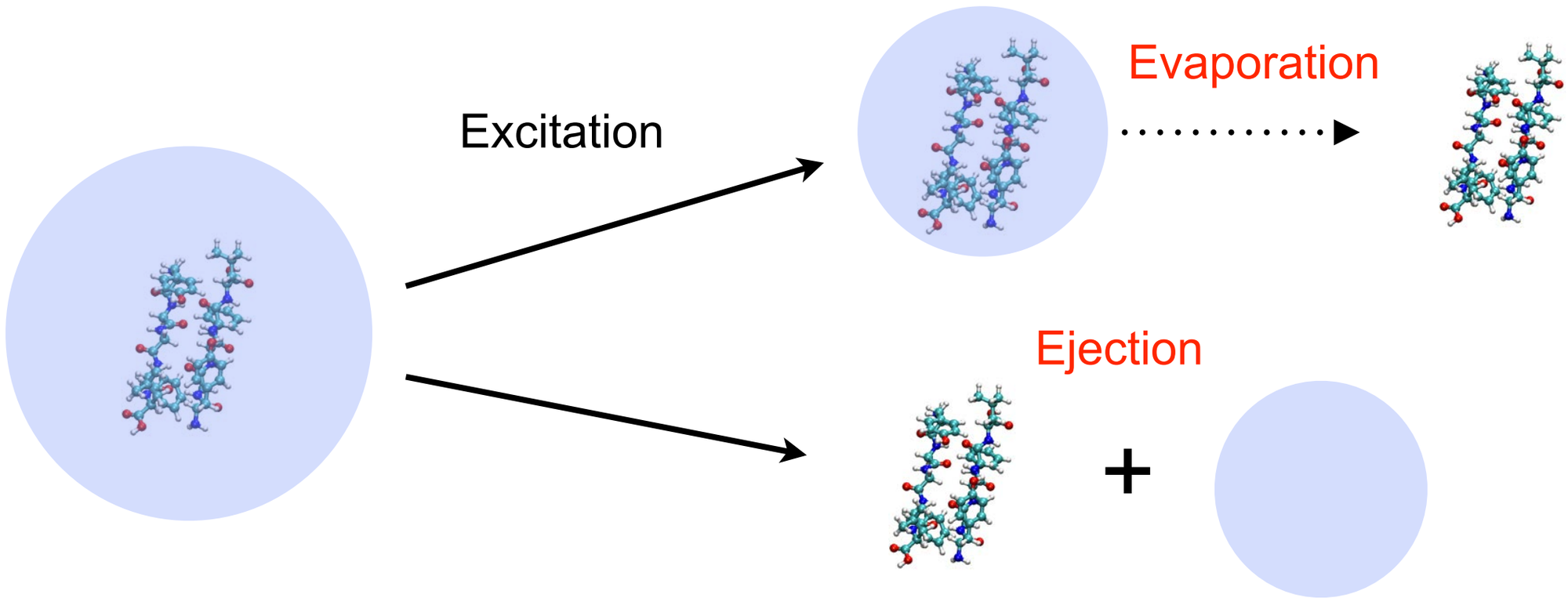
- macro-pulse length > 10 μs
- > 100 mJ / macro-pulse
- 10 – 20 μJ / micro-pulse

- micro-pulse length 0.3 – >5 ps
- FT-limited bandwidth: 0.3 – 5% of central frequency

Action spectroscopy using helium droplets

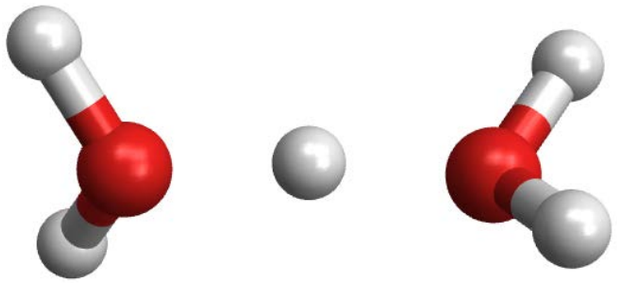
Multiple photon excitation in a macropuls



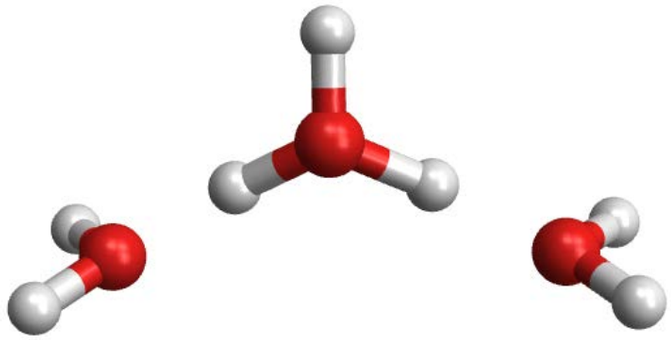


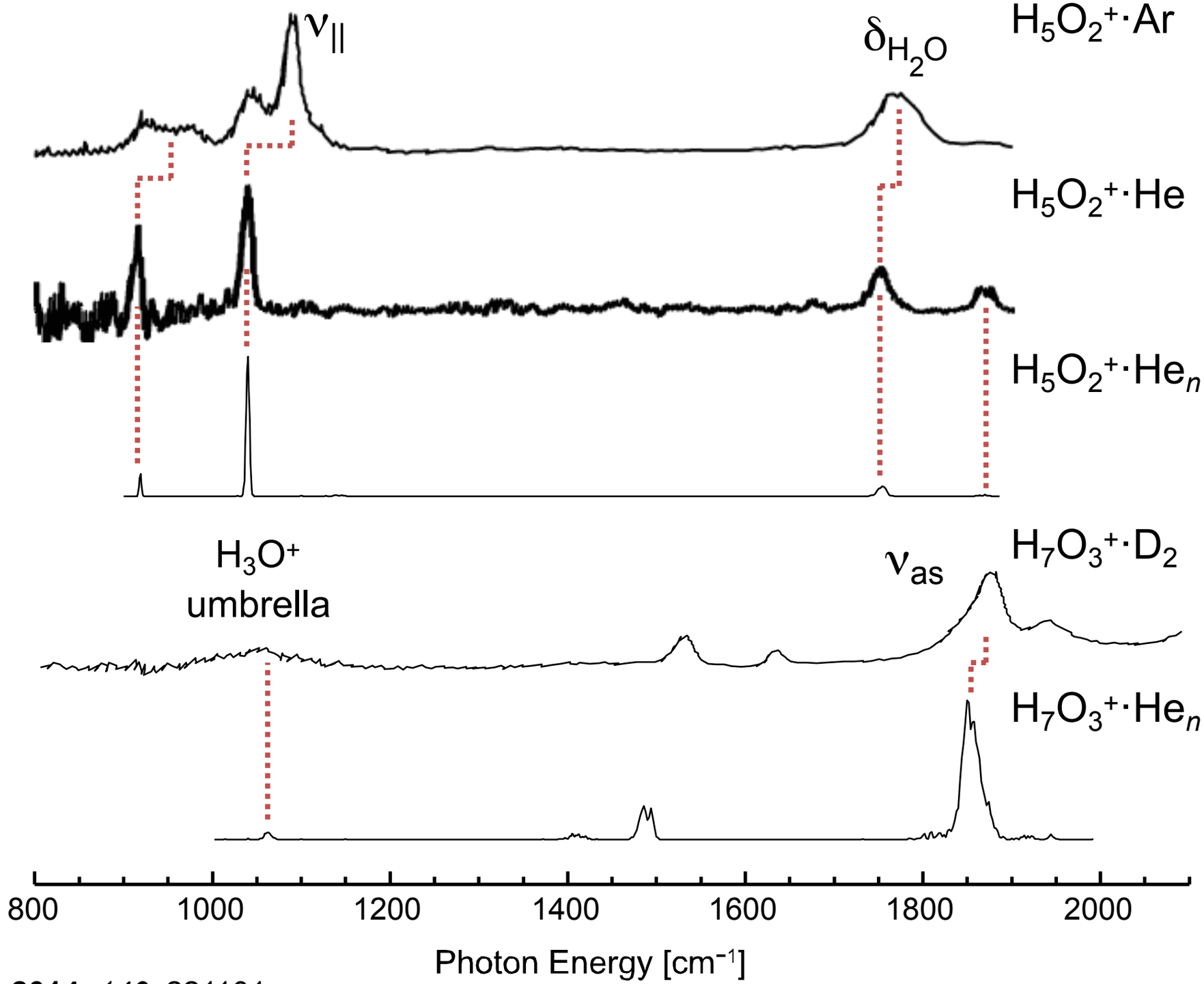
Protonated Water Clusters

$H_5O_2^+$ (Zundel):



$H_7O_3^+$:



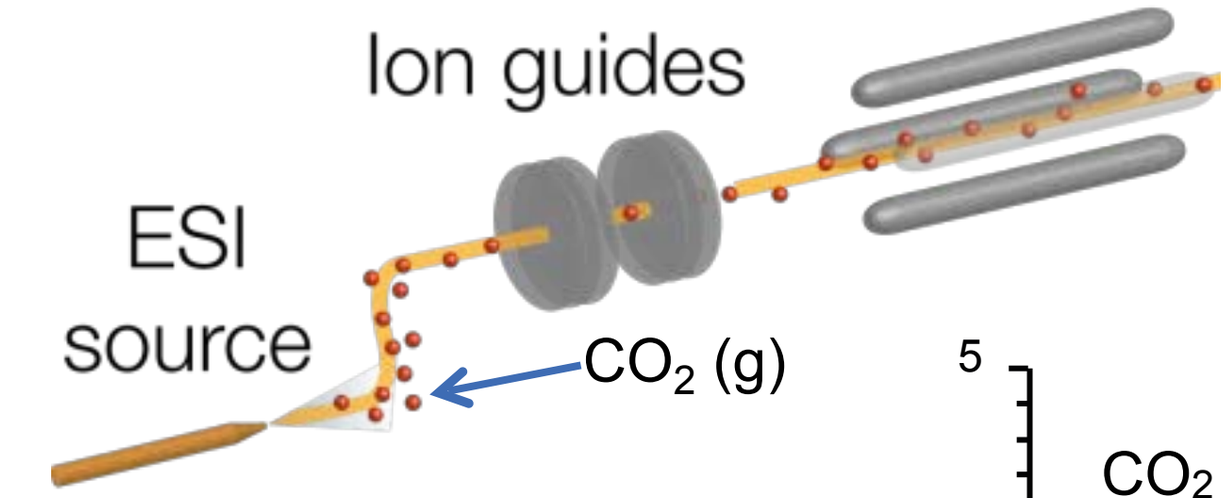


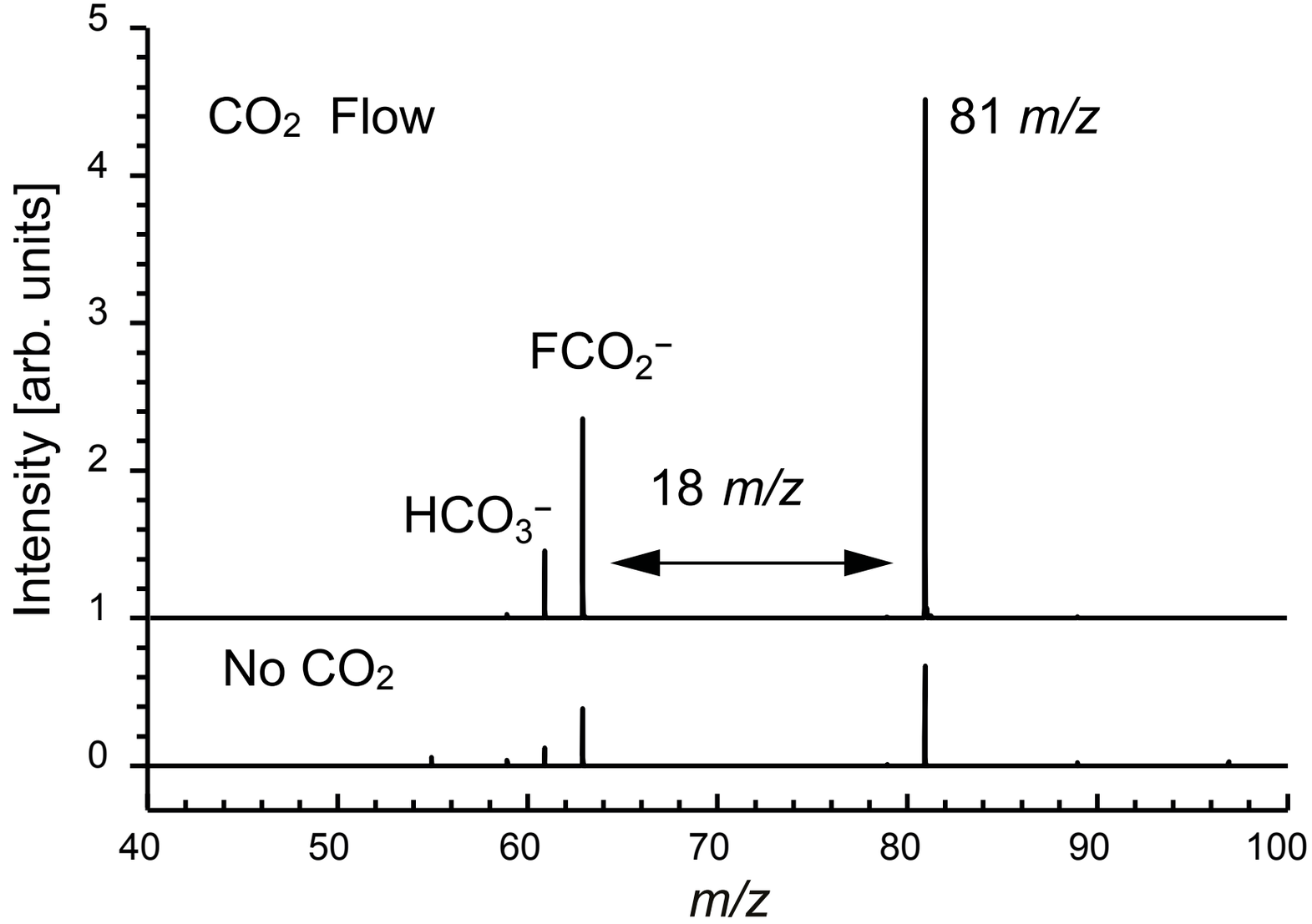
C. J. Johnson *et al.*, *J. Chem. Phys.* **2014**, *140*, 221101.

C. H. Duong *et al.*, *J. Phys. Chem. Lett.* **2017**, *8*, 3782-3789.

Action spectroscopy using helium droplets

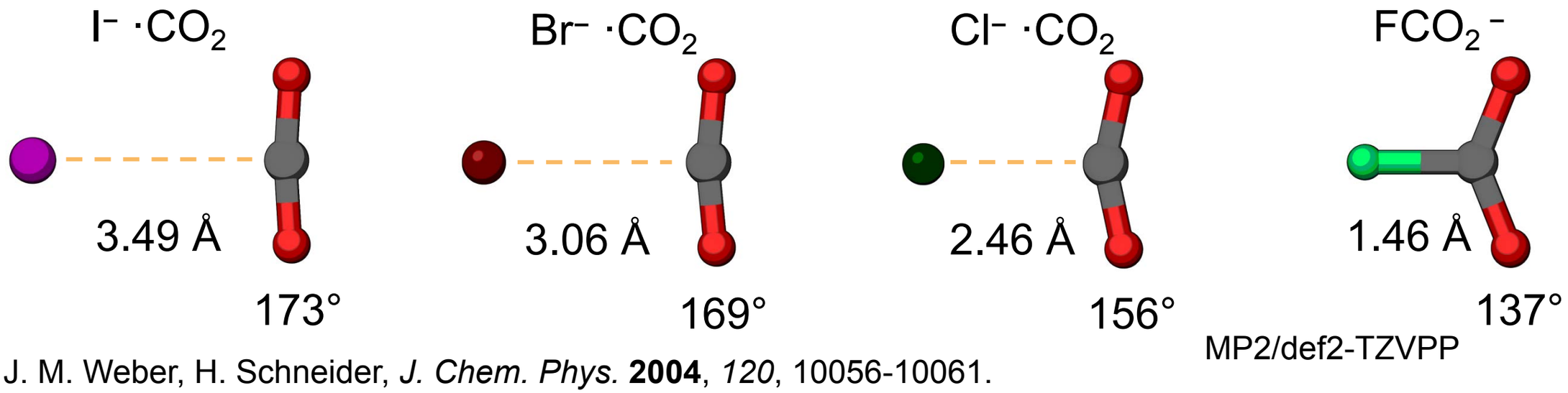
PRODUCTION OF FLUOROFORMATE





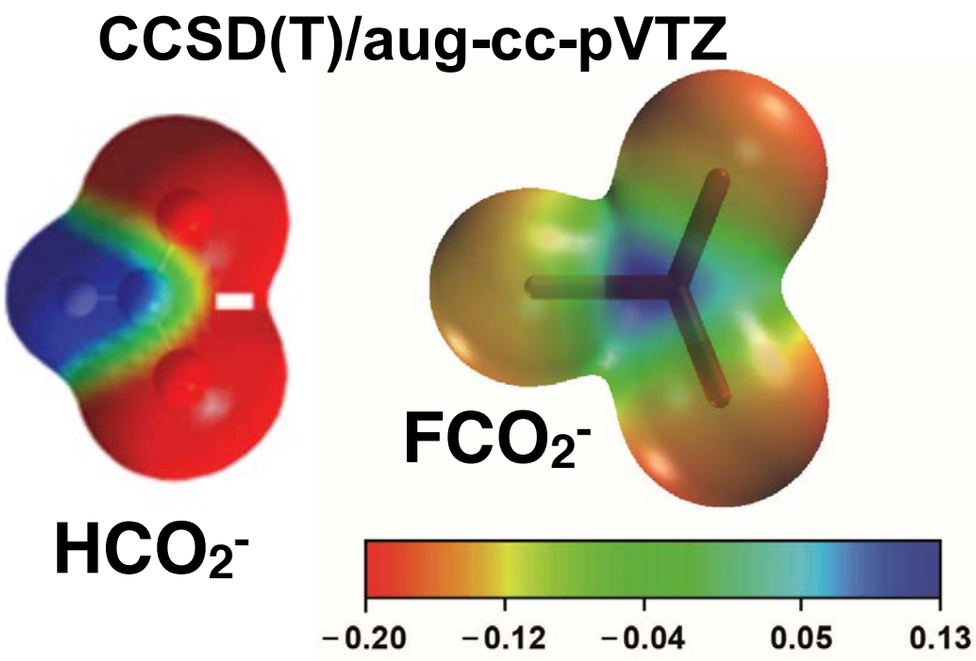
Action spectroscopy using helium droplets

HALIDE–CO_2 COMPLEXES



J. M. Weber, H. Schneider, *J. Chem. Phys.* **2004**, *120*, 10056-10061.

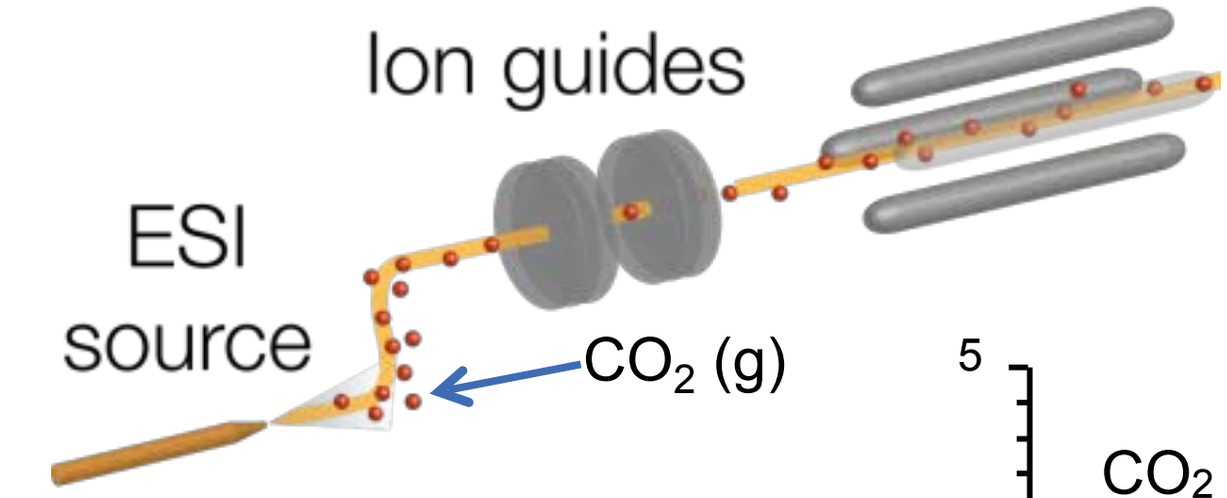
IR Spectroscopy of Fluoroformate

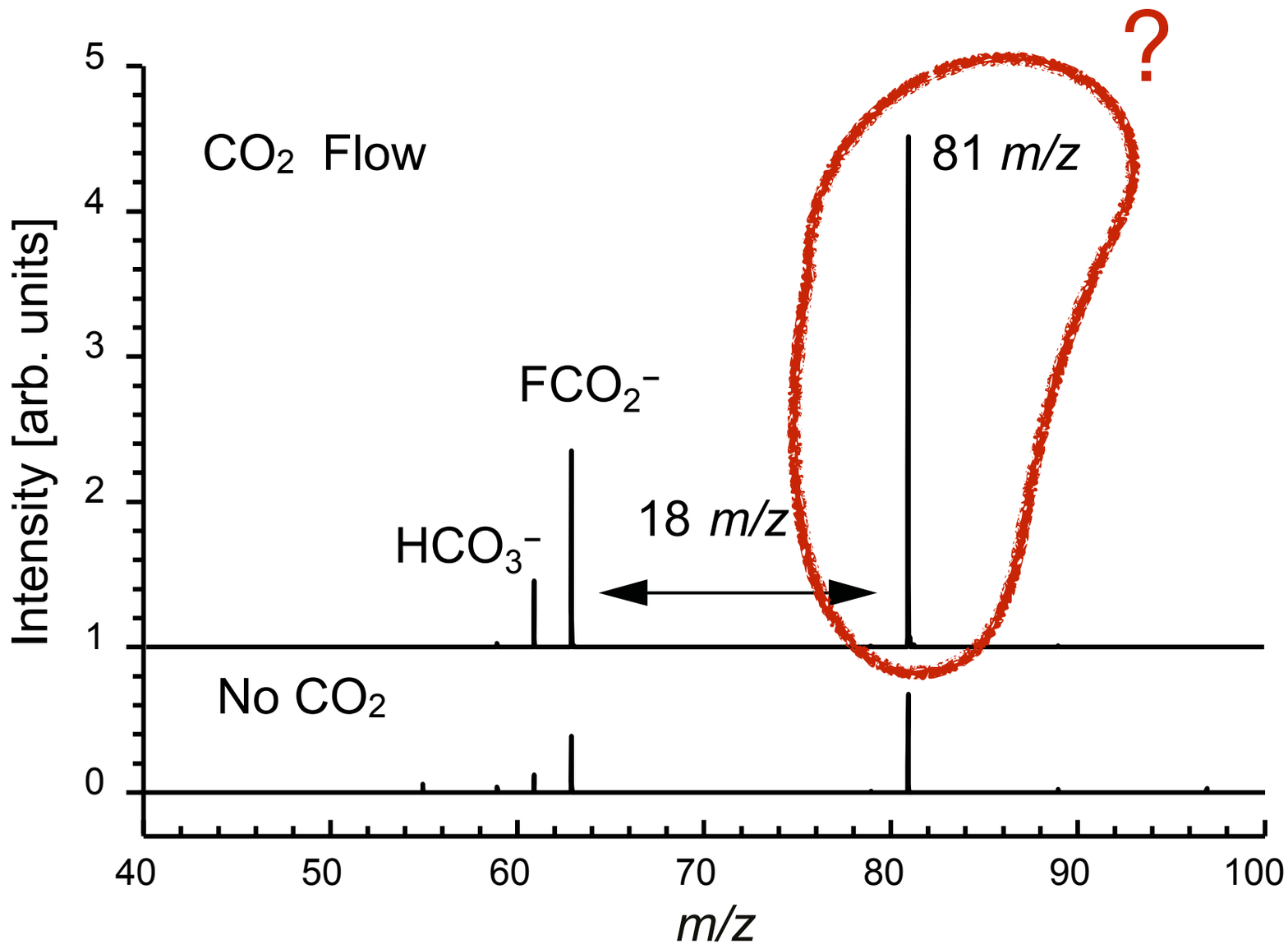


D. A. Thomas, *et al.*, *J. Phys. Chem. Lett.* **2018**, *9*, 2305-2310.

IR Spectroscopy of Fluoroformate

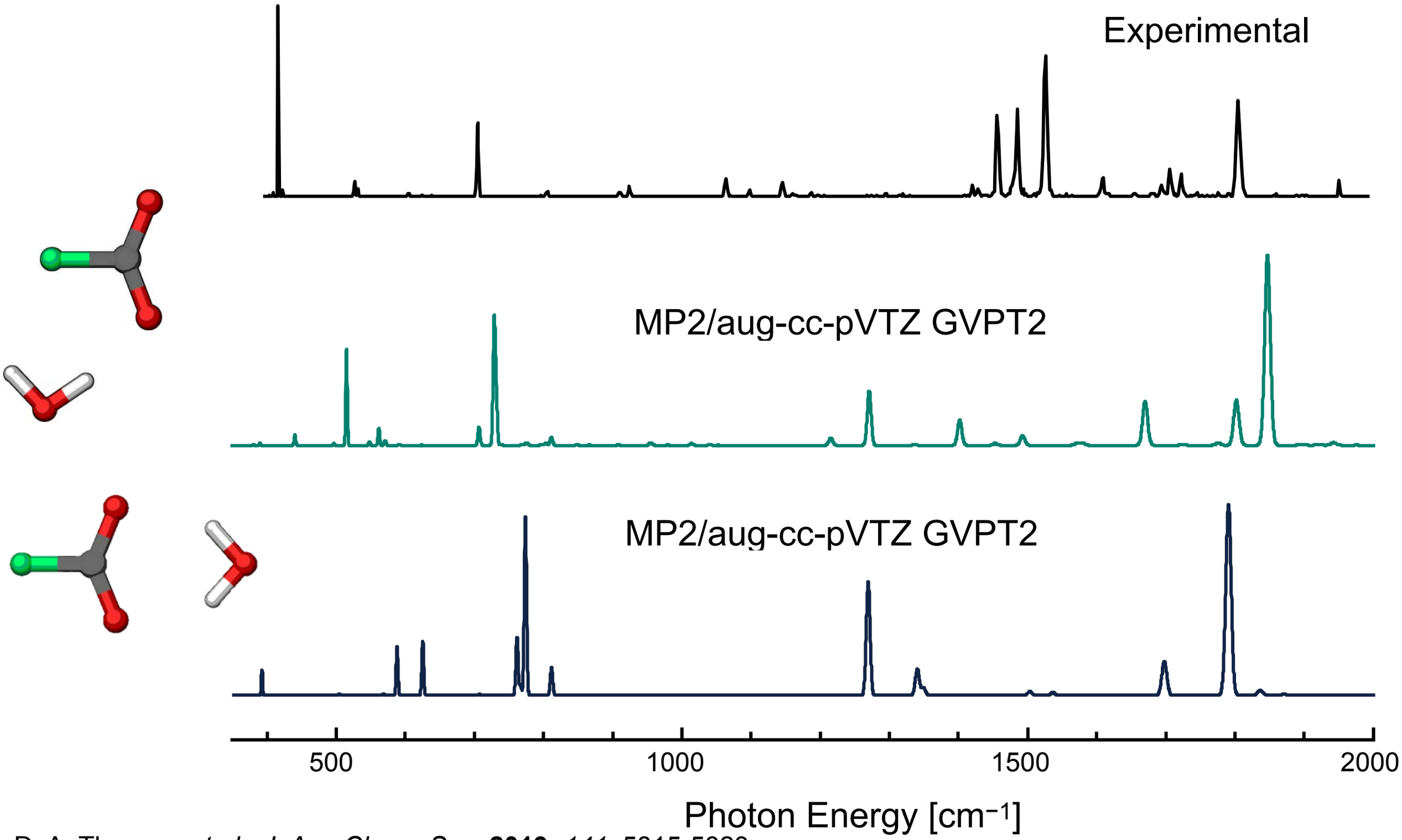
PRODUCTION OF FLUOROFORMATE





IR Spectroscopy of Fluoroformate

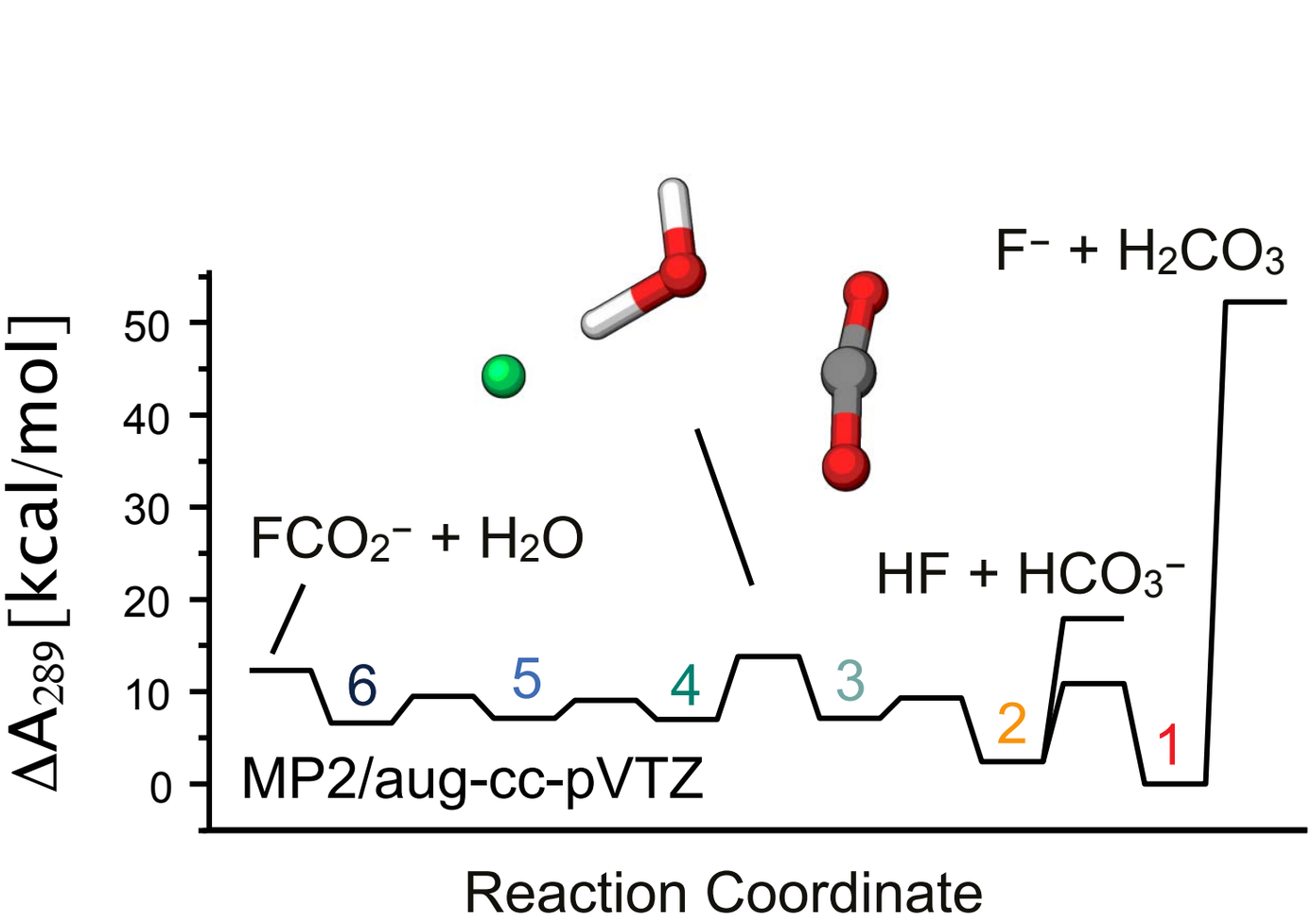
IR SPECTROSCOPY OF FCO_2^- + 18

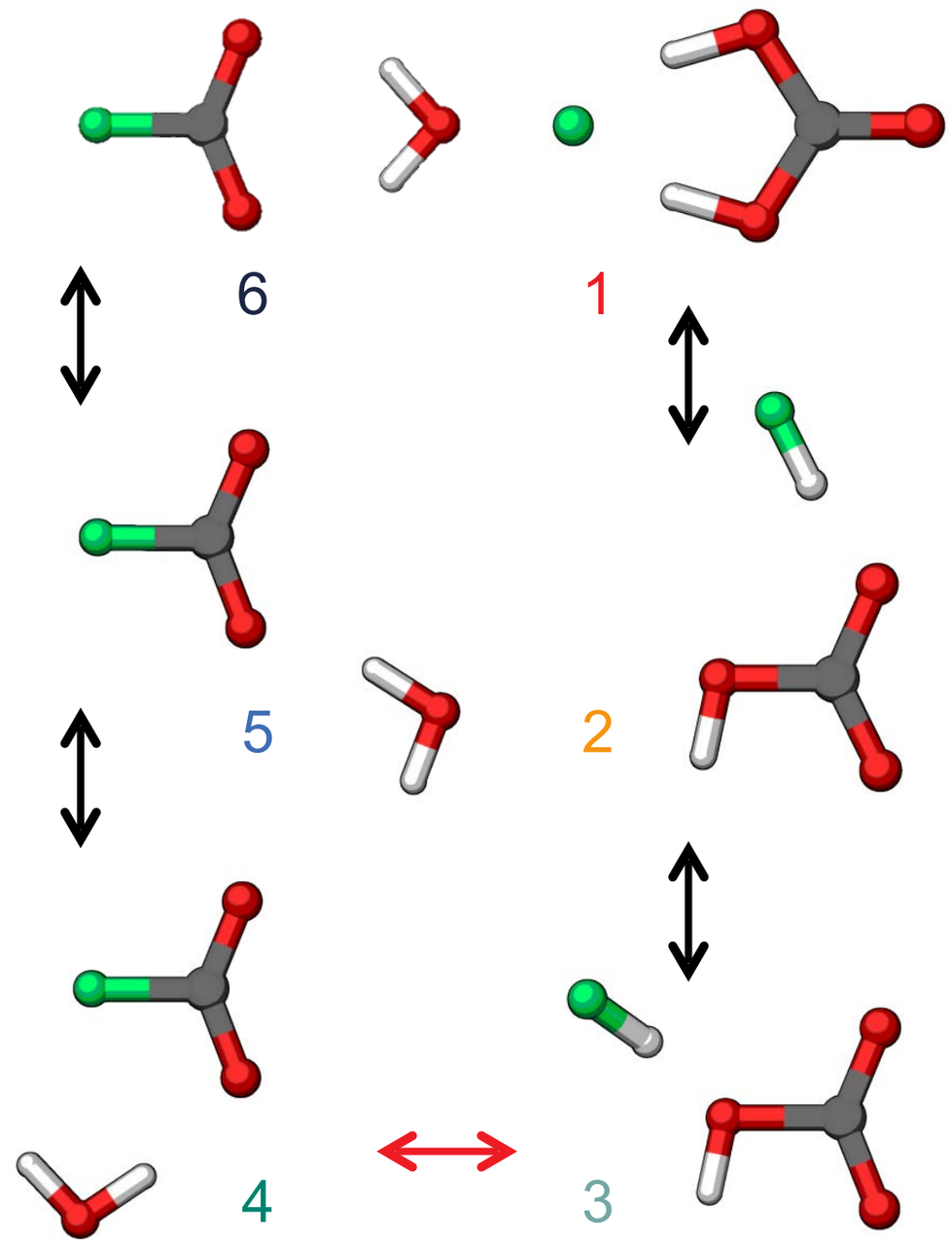


D. A. Thomas, *et al.*, *J. Am. Chem. Soc.* **2019**, *141*, 5815-5823.

Action spectroscopy using helium droplets

REACTION COORDINATE OF FCO_2^- + H_2O

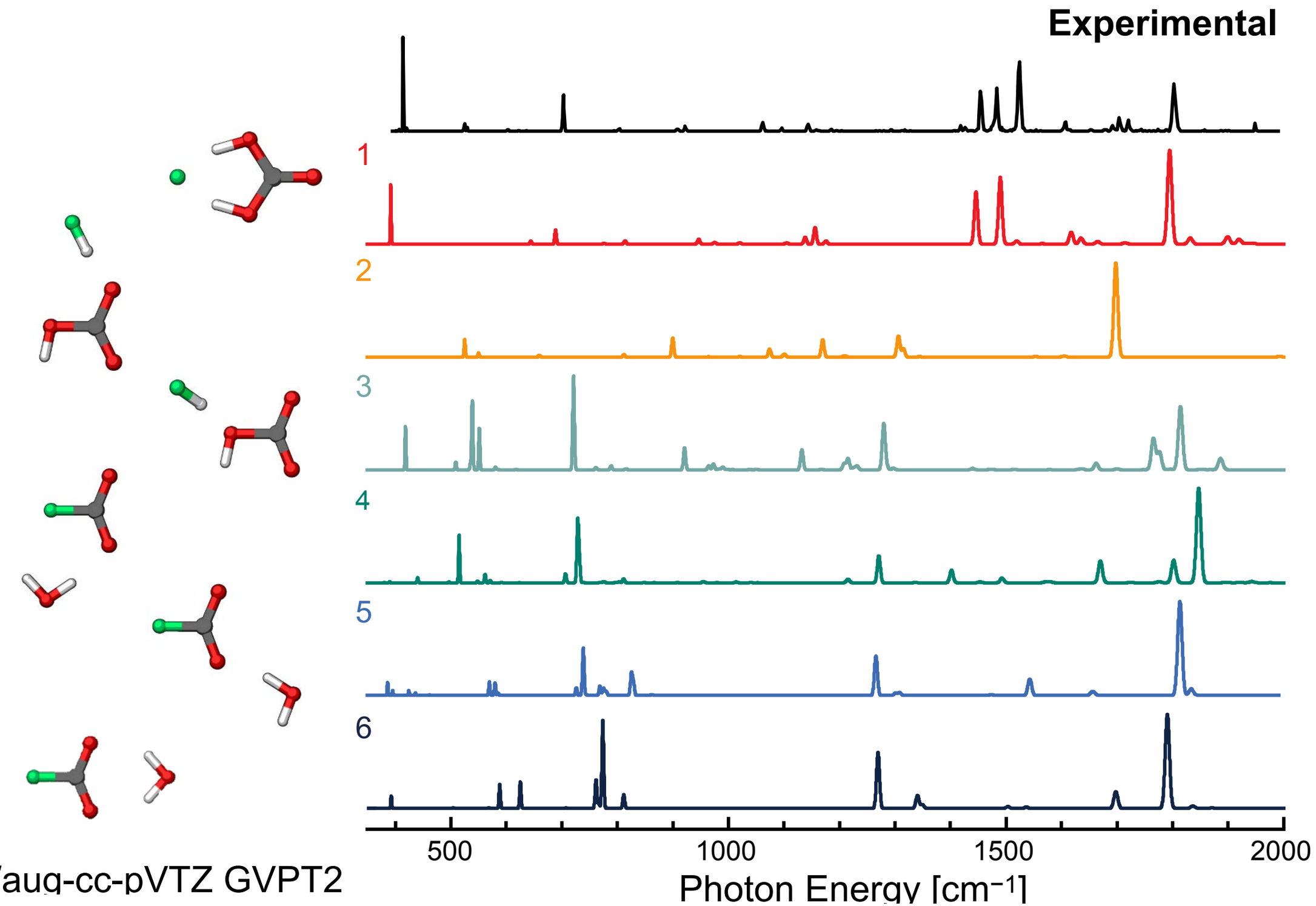




D. A. Thomas, *et al.*, *J. Am. Chem. Soc.* **2019**, *141*, 5815-5823.

Action spectroscopy using helium droplets

IR SPECTROSCOPY OF FCO_2^- + 18

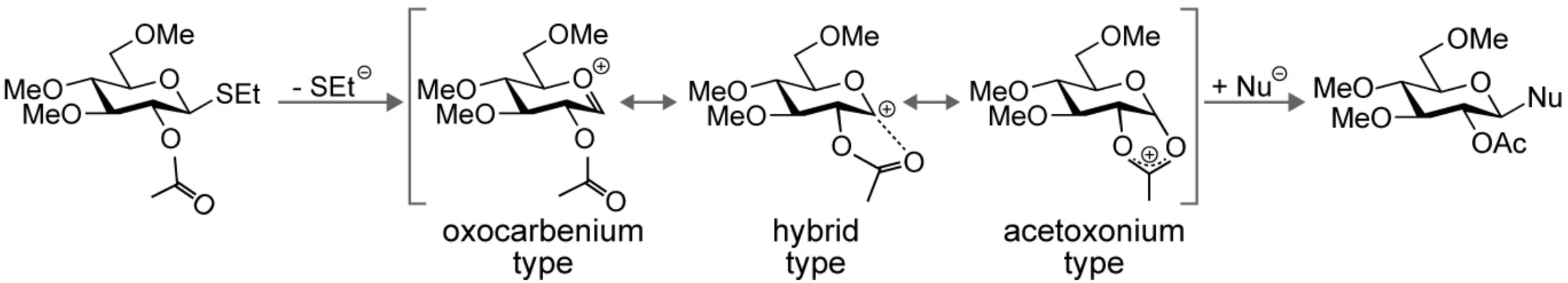


MP2/aug-cc-pVTZ GVPT2

D. A. Thomas, *et al.*, *J. Am. Chem. Soc.* **2019**, *141*, 5815-5823.

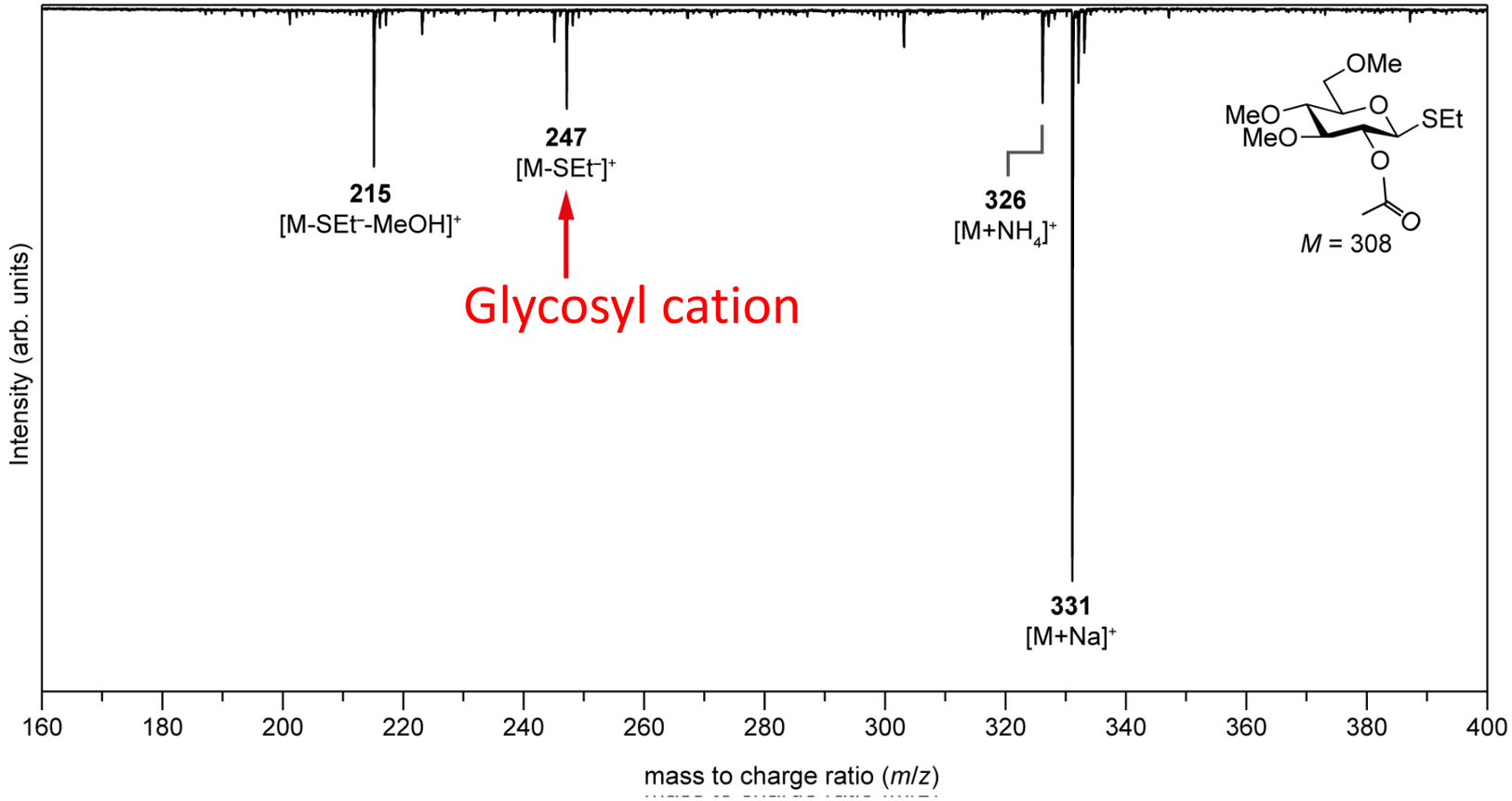
Probing the Structure of Glycosyl Cations

Stereoselective glycosylation reactions:

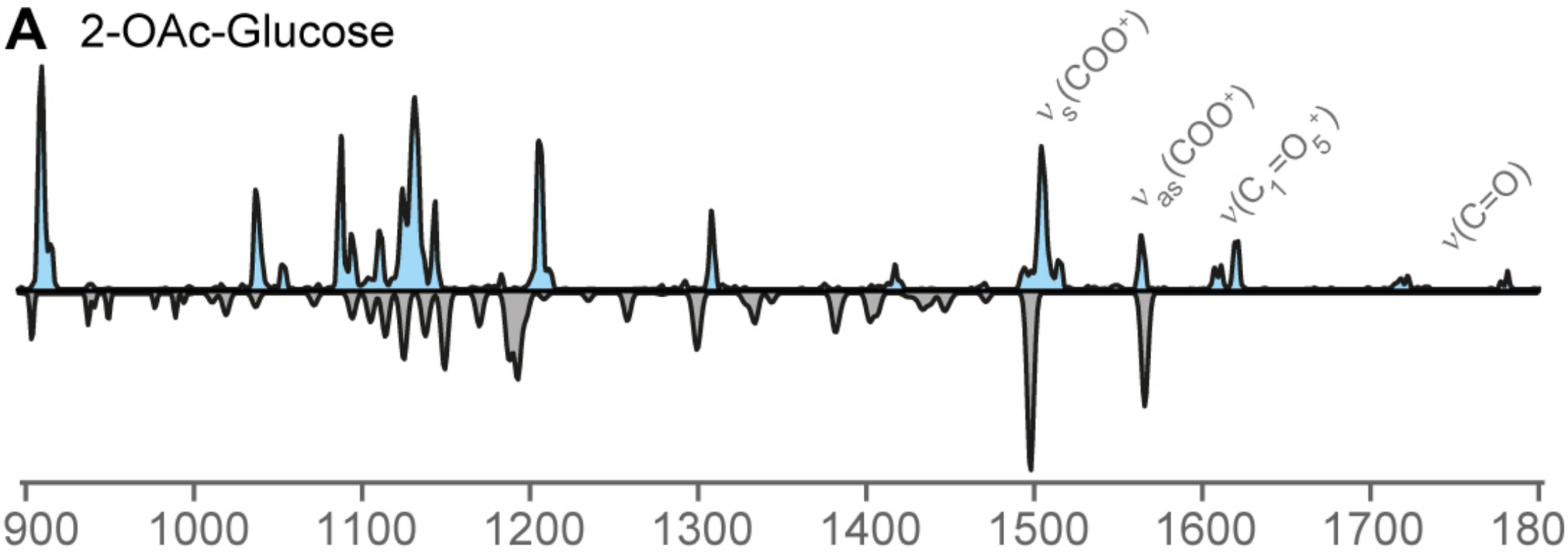


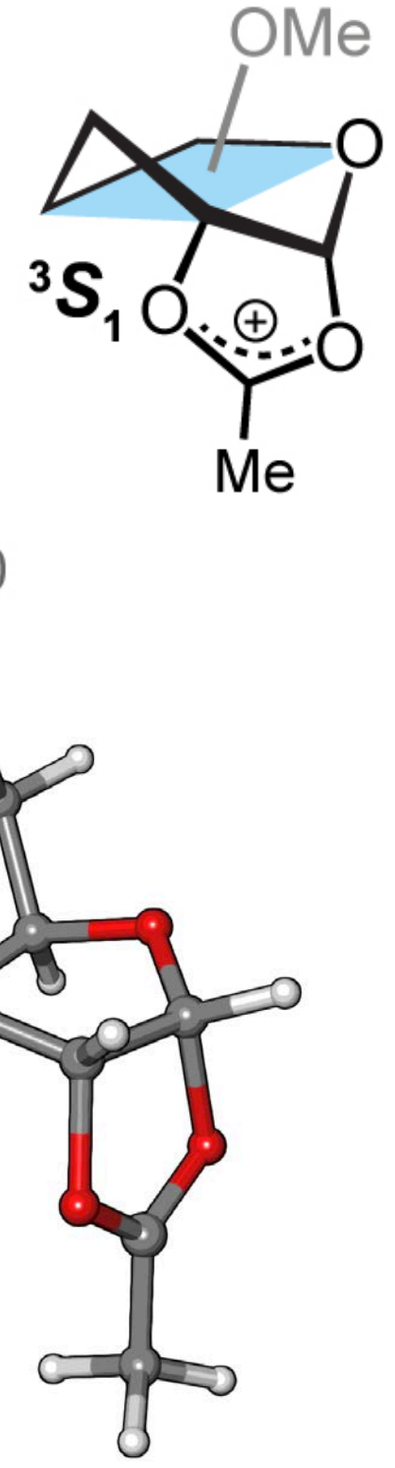
- Short-lived intermediate
- Exact structure unknown
- Too reactive to probe in condensed phase
- Can be isolated as a fragment in the gas phase

Ethyl 2-O-acetyl-3,4,6-tri-O-methyl-1-thio-β-D-glucopyranoside



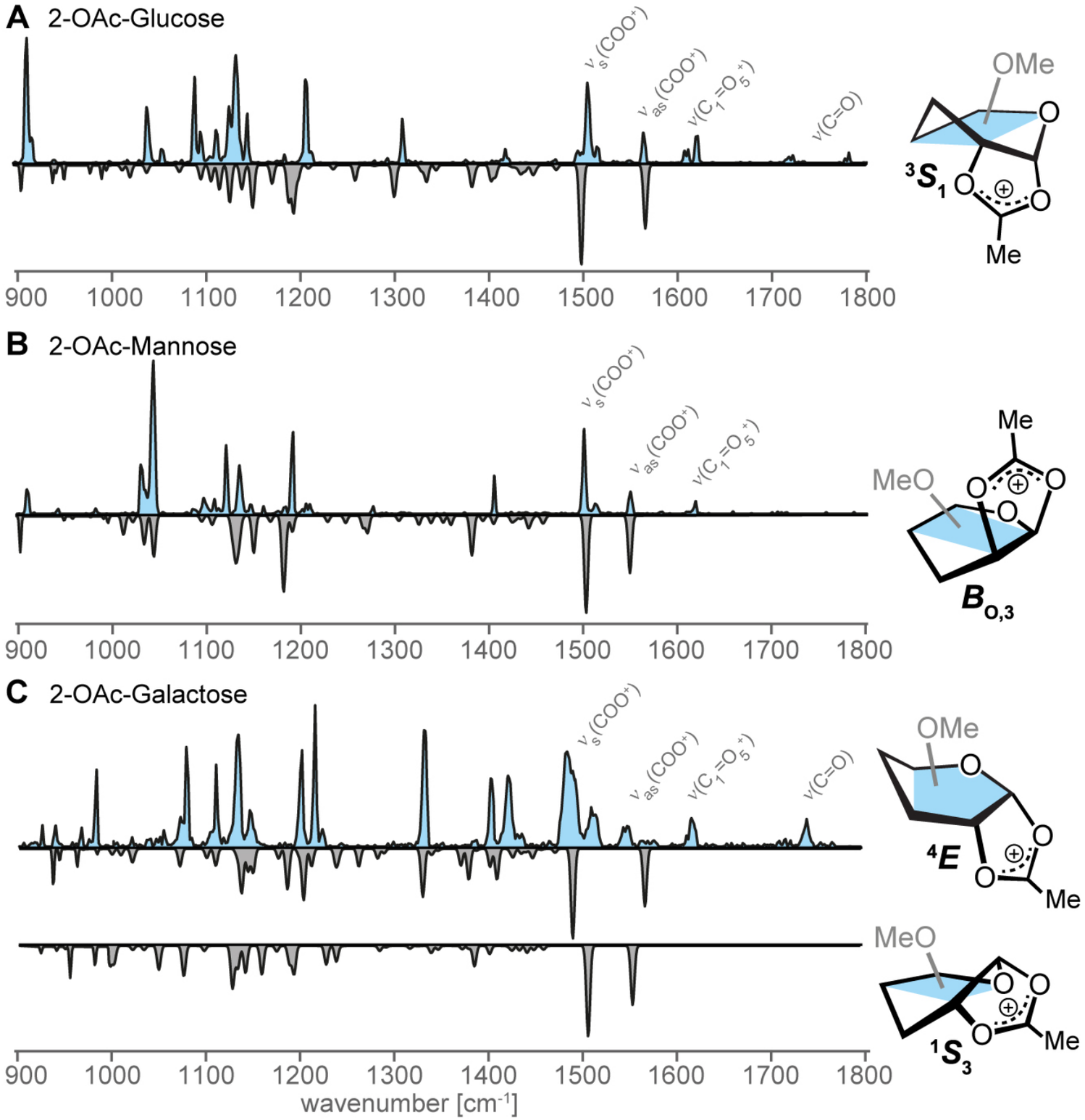
Probing the Structure of Glycosyl Cations





E. Mucha, *et al.*, *Nature Comm.* **2018**, *9*, 4174.

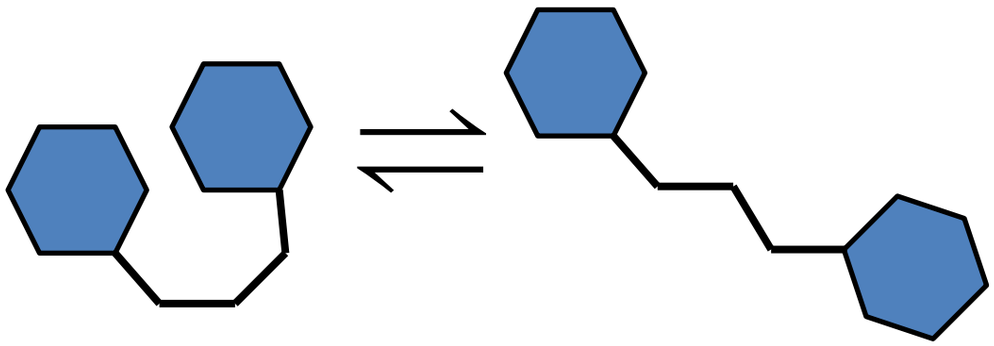
Probing the Structure of Glycosyl Cations



- Highly resolved IR spectra
- Theory provides low energy structure candidates
- Good agreement between theory and experiment
- Ions adopt dioxolenium structures
- Various ring puckers found

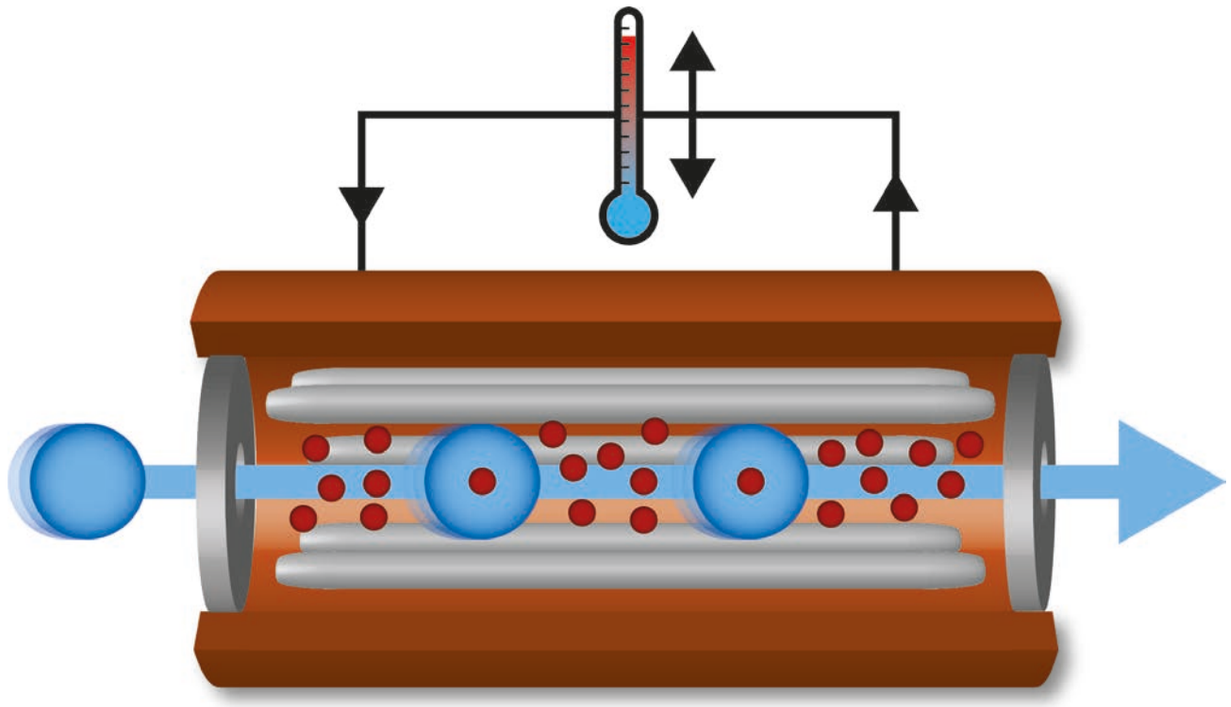
E. Mucha, *et al.*, *Nature Comm.* **2018**, *9*, 4174.

Shock Freezing in Helium Nanodroplets



compact extended

$$\ln K = \ln \frac{[\text{extended}]}{[\text{compact}]} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$

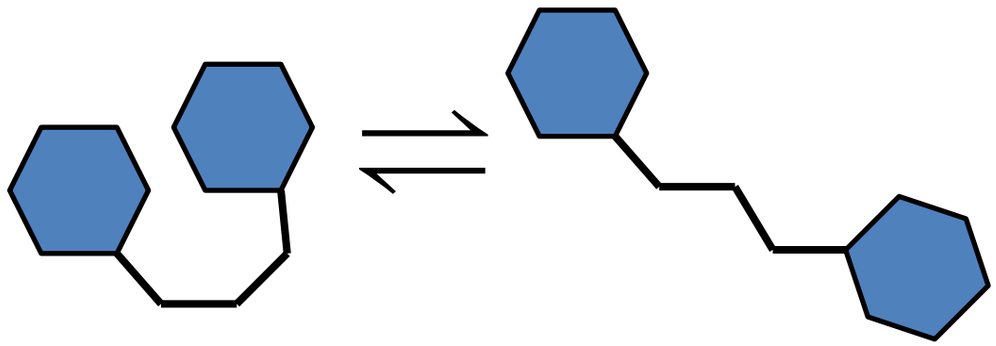


variable-temperature ion trap (80-400 K)

C. M. Leavitt *et al.*, *J. Phys. Chem. A* **2014**, *118*, 9692-9700.

D. S. Skvortsov, A. F. Vilesov, *J. Chem. Phys.* **2009**, *130*, 151101.

Thermochemical Measurements by HENDI IR



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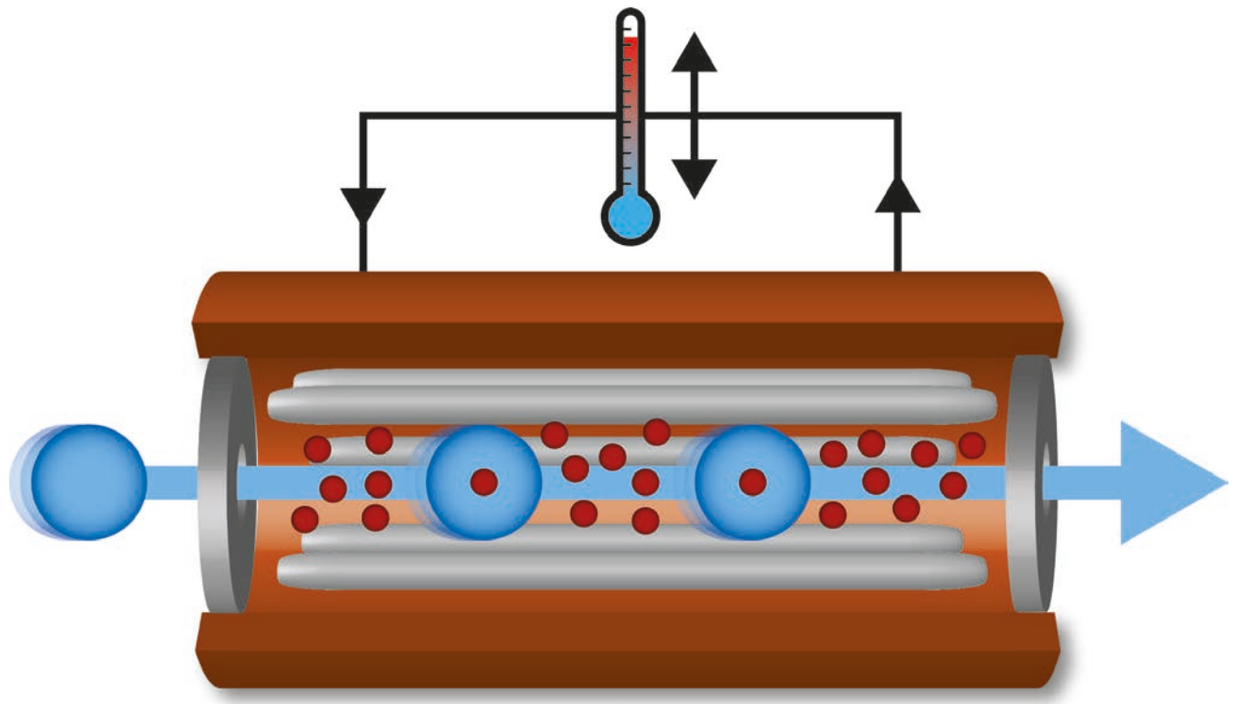
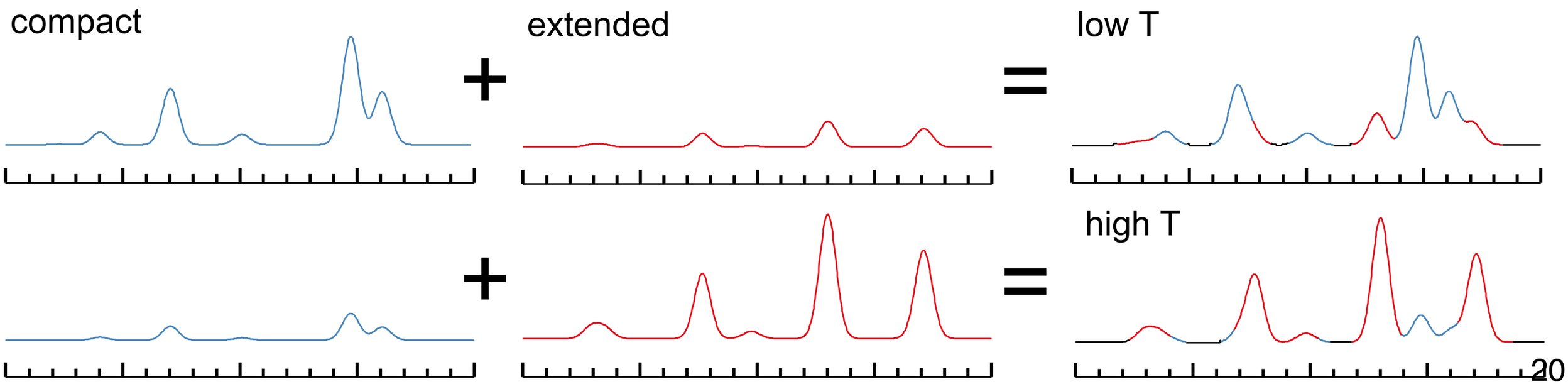
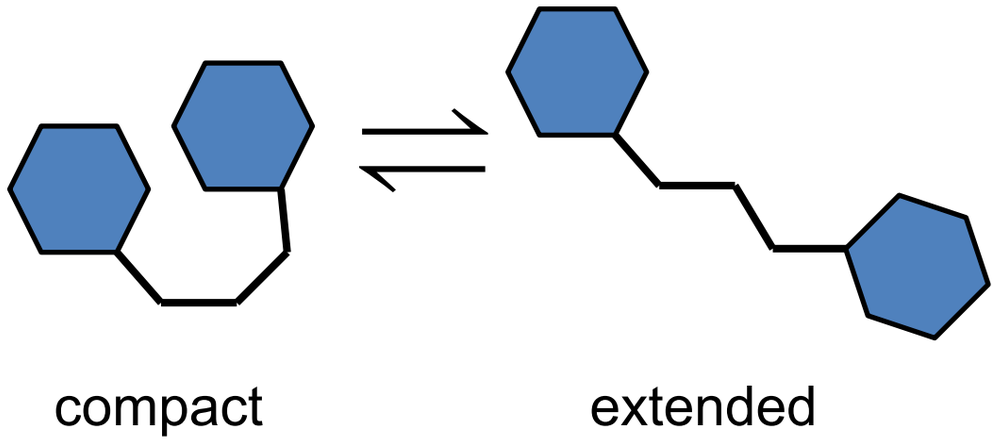


variable-temperature ion trap (80-400 K)



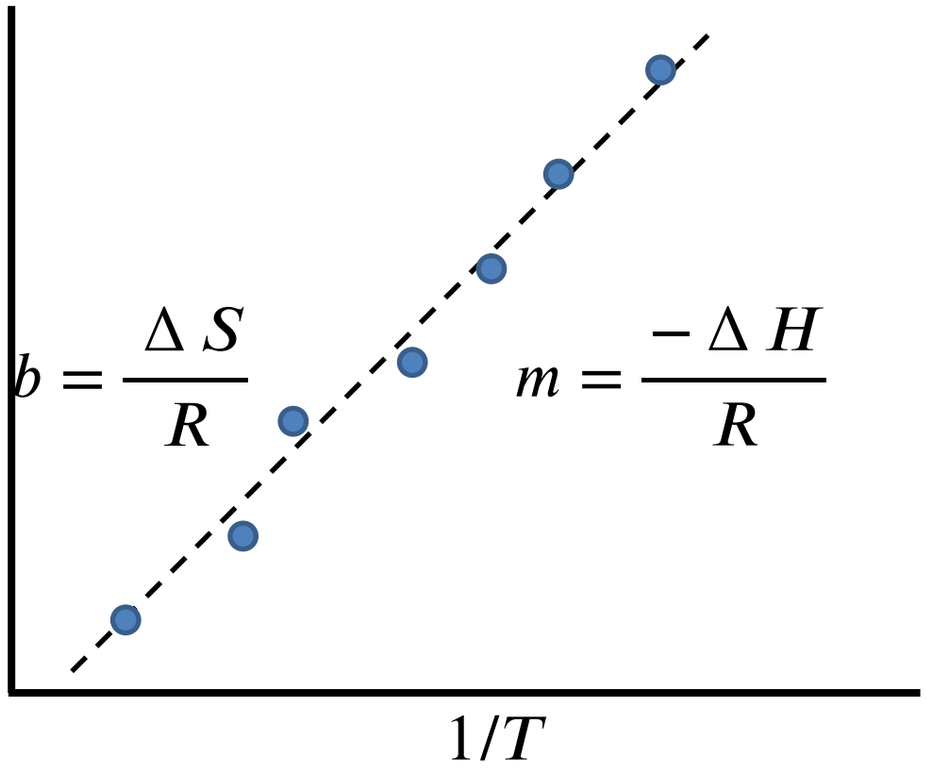
Thermochemical Measurements by HENDI IR

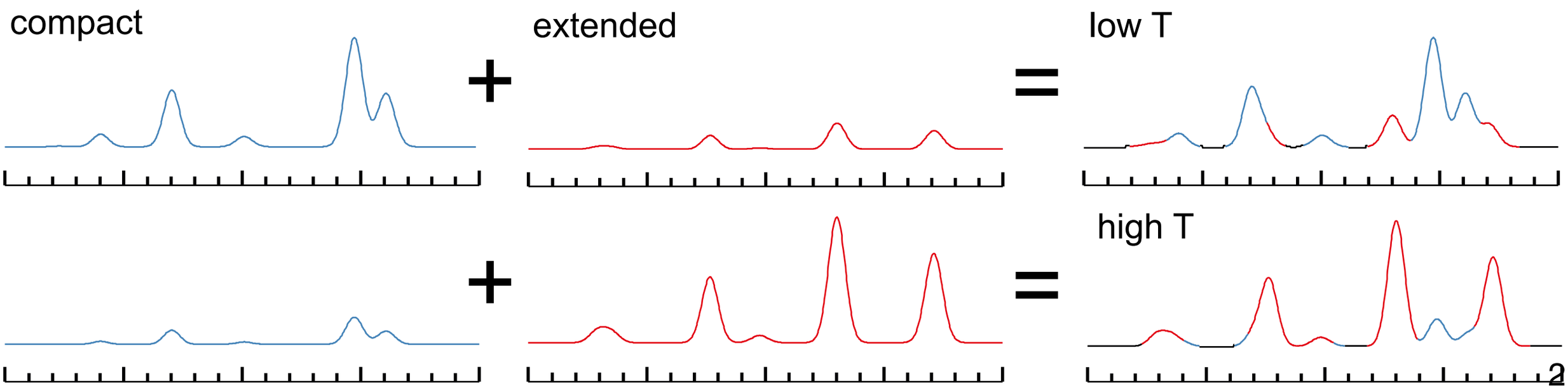


compact ⇌ extended

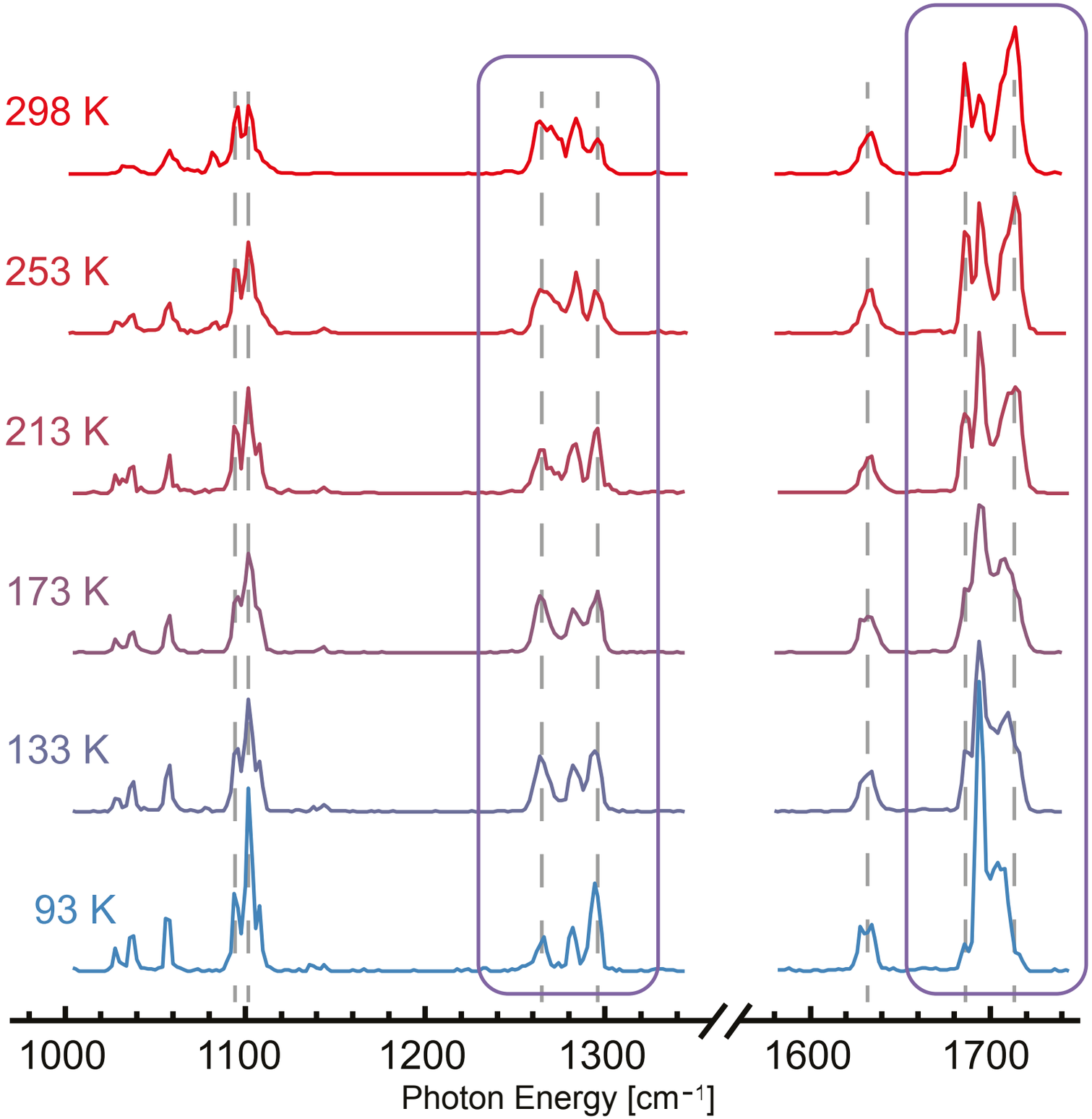
$$\ln\frac{[\text{extended}]}{[\text{compact}]}$$

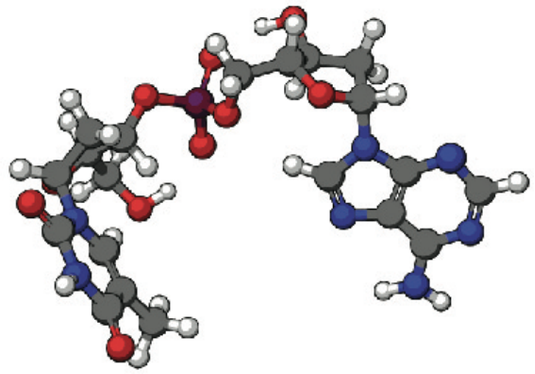
$$\ln K = \ln\frac{[\text{extended}]}{[\text{compact}]} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}$$



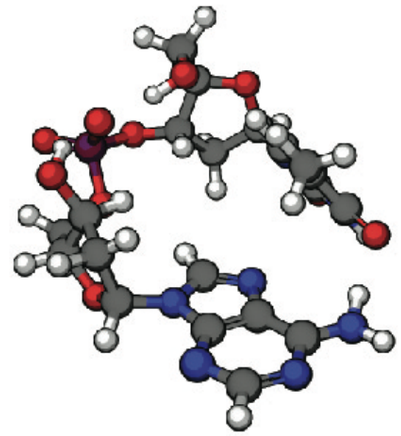


Proof of Principle – Dinucleotide dTpdA

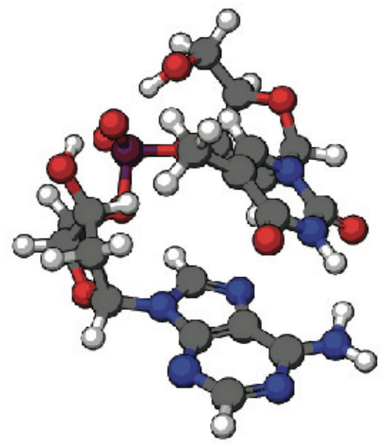




ΔG_{298} = +3.3 kJ mol^{-1} (**3**)

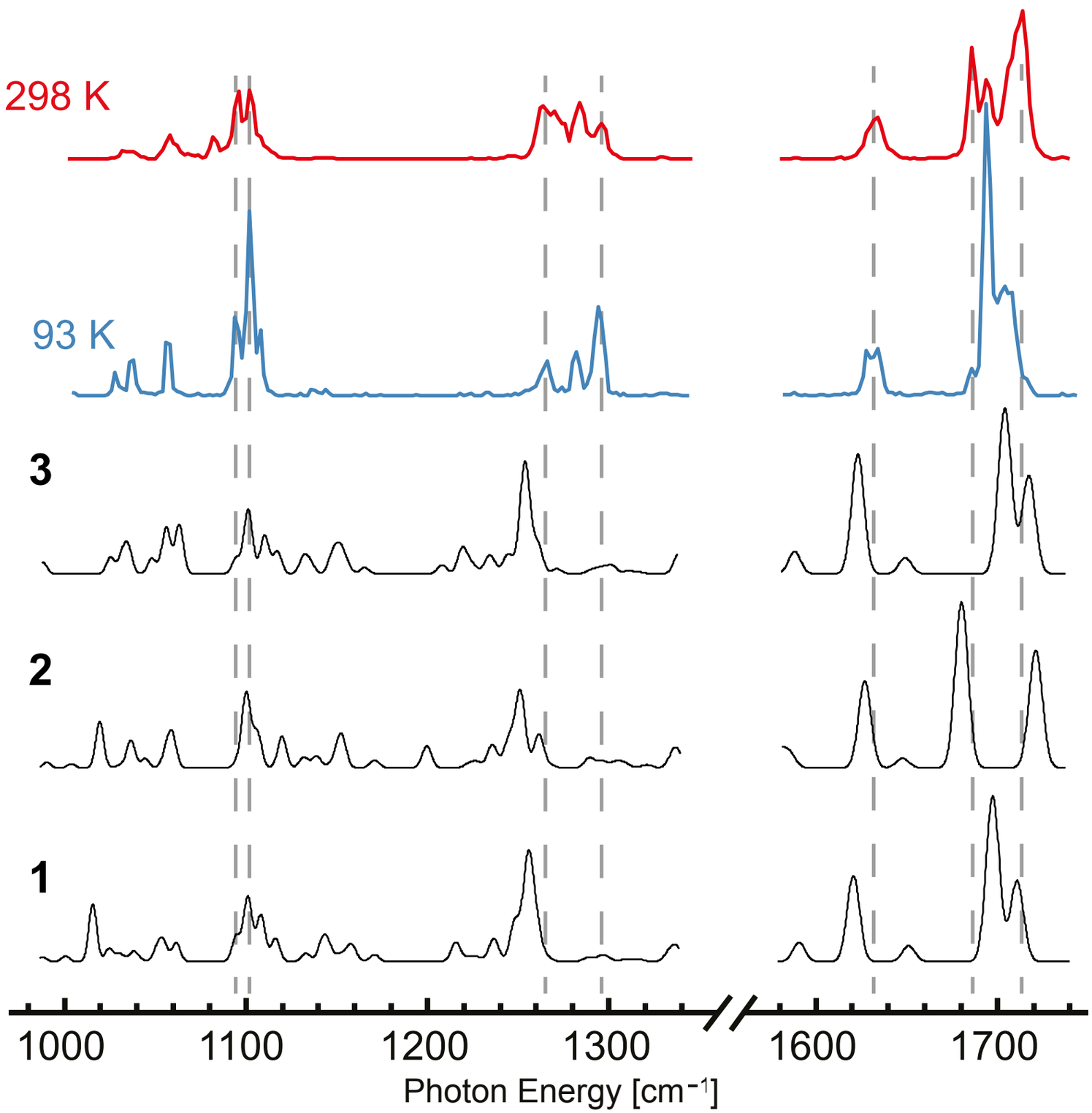


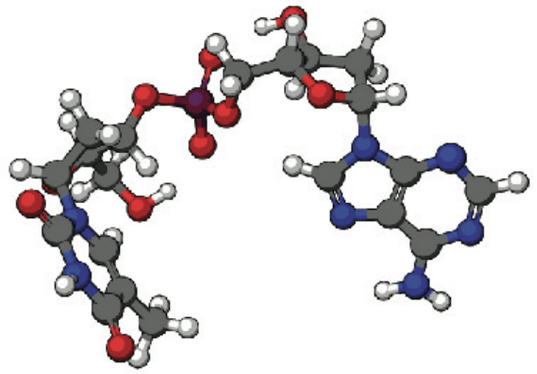
ΔG_{298} = +1.5 kJ mol^{-1} (**2**)



0.0 kJ mol^{-1} (**1**)

Proof of Principle – Dinucleotide dTpdA





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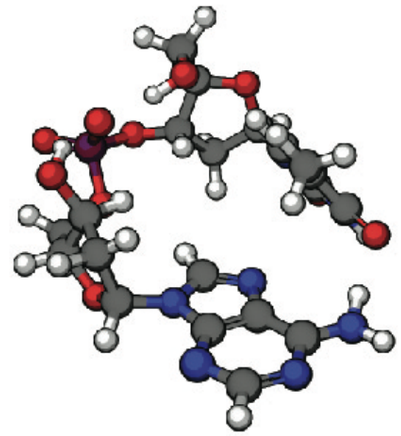

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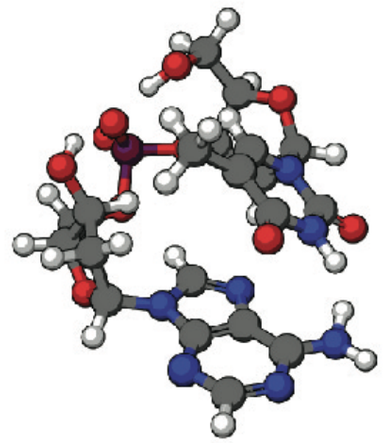

0.0 kJ mol^{-1} (**1**)

Acknowledgements

MP:
Daniel Thomas
Eike Mucha
Mateusz Marianski
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Kevin Pagel

FEL Team:
Wieland Schöllkopf
Sandy Gewinner

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